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FERRIC CHLORIDE LEACH PROCESS: PROGRESS REPORT

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FERRIC CHLORIDE LEACH PROCESS: PROGRESS REPORT

by

B.H. Lucas and D.Y. Shimano

SUMMARY

A novel two-stage ferric chloride leach operation has been developed to:

1) maximize the recovery of lead, zinc, copper and silver values.
2) produce a Zn/SX feed liquor containing a minimum of co-extractable Fe^{3+} values.
3) minimize soluble sulphate values.

Under the optimum conditions, (First stage; 107-108°C, 3.5 M NaCl, 0.43 M HCl, 50 g/L Fe^{3+}, 3.0 H*. Second stage; 107-108°C, 3.5 M NaCl, 0.43 M HCl, 50 g/L Fe^{3+}, 4.5 h) the following was obtained:

1) respective extractions of lead, zinc, copper, and silver of 99.5, 98.3, 93.9, and 91.6 per cent.
2) a liquor for cementation treatment containing from 0.0 to 1.3 g/L Fe^{3+}.
3) conversion of sulphur to soluble sulphate of from 0.91 to 2.4 per cent.

The novel two-stage leach operation has been incorporated into a flowsheet.

The study has demonstrated that:

1) to obtain greater than 95 per cent extraction of copper and silver, further work will be required.
2) a Zn/SX feed liquor containing low residual Fe^{3+} values can be produced, while maintaining good metal extraction.
3) that the cumulative leach residence time of 7.5 h will have to be optimized.
4) that control of soluble sulphate formation will require further work.

It is recommended that additional bench-scale tests be undertaken to address the above problem areas.

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*Leach retention time has not been optimized.

COMPTE RENDU: PROCÉDÉ DE LIXIVIATION DU CHLORURE FERRIQUE

par

B.H. Lucas et D.Y. Shimano

SOMMAIRE

On a exposé une nouvelle méthode pour la lixiviation du chlorure ferrique en deux étapes, afin de:

1) augmenter la récupération de la valeur du plomb, du zinc, du cuivre et de l'argent.
2) produire une liqueur d'alimentation du Zn/Sx qui contient un minimum en co-extraction des valeurs du Fe^{3+}.
3) dimineur les valeurs du sulfate soluble.

On a obtenu sous conditions optimums (dans la 1ère étape: 107-108°C, 3,5 MNaCl, 0,43 MHCl, 50 g/L Fe^{3+}, 3,H*; dans la 2e étape: 107-108°C, 3,5 MNaCl, 0,43 MHCl, 50 g/L Fe^{3+}, 4,5 h) les résultats suivants:

1) des extractions de plomb, de zinc, de cuivre et d'argent de 99,5%; 98,3%; 93,9% et 91,6% respectivement;
2) une liqueur pour le traitement au ciment ayant de 0,0 à 1,3 g/L Fe^{3+};
3) la conversion du soufre en sulfate soluble de 0,91% à 2,4%.

On a incorporé la nouvelle méthode de lixiviation en deux étapes dans le schema de traitement.

Les observations ont montré que:

1) on demandera plus de travail afin d'obtenir plus de 95% dans l'extraction du cuivre et de l'argent;
2) on peut produire une liqueur d'alimentation Zn/Sx ayant un bas résidu en valeurs du Fe^{3+}, lorsqu' on mantient une bonne extraction du métal;

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*Le séjour de retention n'a pas été optimisé

3. on doit optimiser le temps de séjour cumulatif de la lixiviation de 7,5 h;
4. on demandera davantage de travail dans le contrôle de formation du sulfate soluble.

On recommande de poursuivre des essais additionnels faits au laboratoire, afin de faire face aux problèmes signalés ci-dessus.

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INTRODUCTION

PREVIOUS WORK

Although New Brunswick has the largest reserves of zinc, lead and silver in Canada, the economic exploitability of these resources has been severely hampered by the complexity of the orebodies (1). It has been demonstrated that high recoveries, which are essential for the economic viability of many of the N.B. deposits, can only be achieved through the production of bulk concentrates (2), which because of their complexity and relatively low grade, are not amenable to conventional extraction and refining processes. It is essential therefore to develop a new extraction process which will economically recover the zinc, lead, copper, silver and other saleable byproducts from the bulk concentrates, while minimizing environmental problems associated with the removal and/or disposal of pyrite and SO_2. The processes chosen for development and evaluation are those deemed to be the most likely to achieve commercial acceptance in the short to medium term. One of CANMET's roles is to contribute to the development and evaluation of a ferric chloride leach (FCL) process. The Leaching Section of the Extractive Metallurgy Laboratory has undertaken the technical evaluation of the FCL process (leaching, S/L separation, leachant regeneration and recovery of Pb, Ag and Cu byproducts). This report is concerned mainly with the ferric chloride leach stage aimed at the recovery of at least 95% of the non-ferrous metal values from a representative Zn/Pb/Cu/Ag bulk concentrate.

The knowledge acquired from these studies will allow federal and provincial governments to formulate policies and programs to facilitate the orderly development of ore deposits not presently being exploited, and to improve the overall utilization of those deposits presently being mined. Successful development of an extraction process will lead to increased economic growth, and employment in N.B., and add value to Canadian exports. Direct benefits could accrue to companies which presently have base metal properties in N.B. such as Anaconda, Cominco, Placer Development, Brunswick Mining and Smelting, Heath Steele and Sullivan Corporation. Benefits could also accrue to companies with similar deposits elsewhere such as HBMS, Kidd Creek, and Cyprus Anvil.

Dutrizac et al. of CANMET have studied $FeCl_3$ leaching on individual minerals and on a bulk concentrate (3,4,5). The pilot plant development

work and subsequent bench-scale tests presented in this report are an extension of Dutrizac's bench-scale study on bulk concentrate to which detailed reference is made later. A similar but much more extensive program involving pilot-plant operations on all aspects of the $FeCl_3$ Leach Process including product recovery has been pursued by the USBM using chalcopyrite concentrate (6,7,8) and galena concentrate (9,10). Various aspects of the USBM flowsheet are also referred to later in the text.

As the program evolved from single-stage to 2-stage counter current $FeCl_3$ leaching, a pilot-plant program by Elkem-Spigerverket A/S, Norway (11,12), $FeCl_3$ leaching of McArthur River Zn-Pb sulphide concentrate (13), $CuCl_2$ leaching of a complex Cu/Zn/Pb ore (14), and a Cl_2-O_2 leaching technique by the USBM (15) gave some insight into improving metal extractions, soluble copper precipitation and sulphate formation.

BENCH-SCALE LEACH TEST - A

Dutrizac has studied the single-stage $FeCl_3$ leaching of a bulk concentrate (5). In this study he observed the effect of $FeCl_3$ concentration, concentrate to $FeCl_3$ ratio, HCl concentration, agitation and temperature. Galena was observed to be readily soluble, whereas the sphalerite and chalcopyrite leaching rates increased with increasing $FeCl_3$ concentration. The optimum liquid/solid ratio was 2 L of 2.0 M $FeCl_3$/325 g concentrate. Zinc, copper and silver extractions all increased with increasing temperature, while chalcopyrite (Cu) and tetrahedrite (Ag) dissolutions were particularly temperature sensitive. HCl concentration was not a critical variable with respect to the solubilization of the Pb, Zn, Cu, and Ag values but enough acid was necessary to prevent iron precipitation via hydrolysis. Agitation was not a factor in the rate of metal dissolution and was required only to suspend the solids in solution. The order of mineral activity was given as galena > sphalerite > chalcopyrite.

Extractions of 95% Zn, 99.5% Pb, 85% Cu and 85% Ag were achieved under the following preferred conditions:

162 g bulk concentrate/L of 2 M $FeCl_3$
Temperature = 103°C
Atmospheric pressure
Retention = 5 h

From this bench study Dutrizac and Craigen devised the conceptual flowsheet as shown in Figure 1. After a first stage leach and a hot liquid/solid separation, the leach liquor would be contacted with excess fresh concentrate feed in order to neutralize any residual ferric iron. Ferric iron is deleterious to the subsequent cementation step as Fe^{3+} values consume Pb powder.

First Pilot-Plant Leach

Prior to the pilot plant, further bench tests were done to confirm the optimum conditions. Bulk concentrate was leached at 13% solids in 2 M $FeCl_3$. Temperature was maintained at 104-105°C for 4 hours. The leach slurry was filtered and the residue washed with hot water (90°C) three times at L/S ratio of 4:1. Metal extractions were:

Pb = 99.5%

Zn = 98.0%

Cu = 95.4%

In the first pilot plant, a steam-jacketed teflon-coated SS 57 L tank with no baffles and a rubber-coated marine impeller were used. A condenser was added to the leach vessel to maintain the slurry density. The following leach conditions were used in the first stage:

Bulk concentrate = 10.12 Kg

2 M $FeCl_3$ liquor = 51.75 L

HCl = 0.35 M

Temperature = 104-105°C

Retention = 4 h

Wash = H_2O (90°C) 3-displacements of 4.5 L each on pressurized pan filter

Table 1 shows the chemical analyses of the feed concentrate which is finely sized at 86.9 wt % - 44 µm and 76.4 wt % - 37 µm.

Table 1. Chemical analyses of CANMET bulk concentrate (wt %)

Pb	8.75	Fe	19.1
Zn	28.1	Ag	233 g/t
Cu	0.78	S_T	35.0
		S/SO_4	1.51

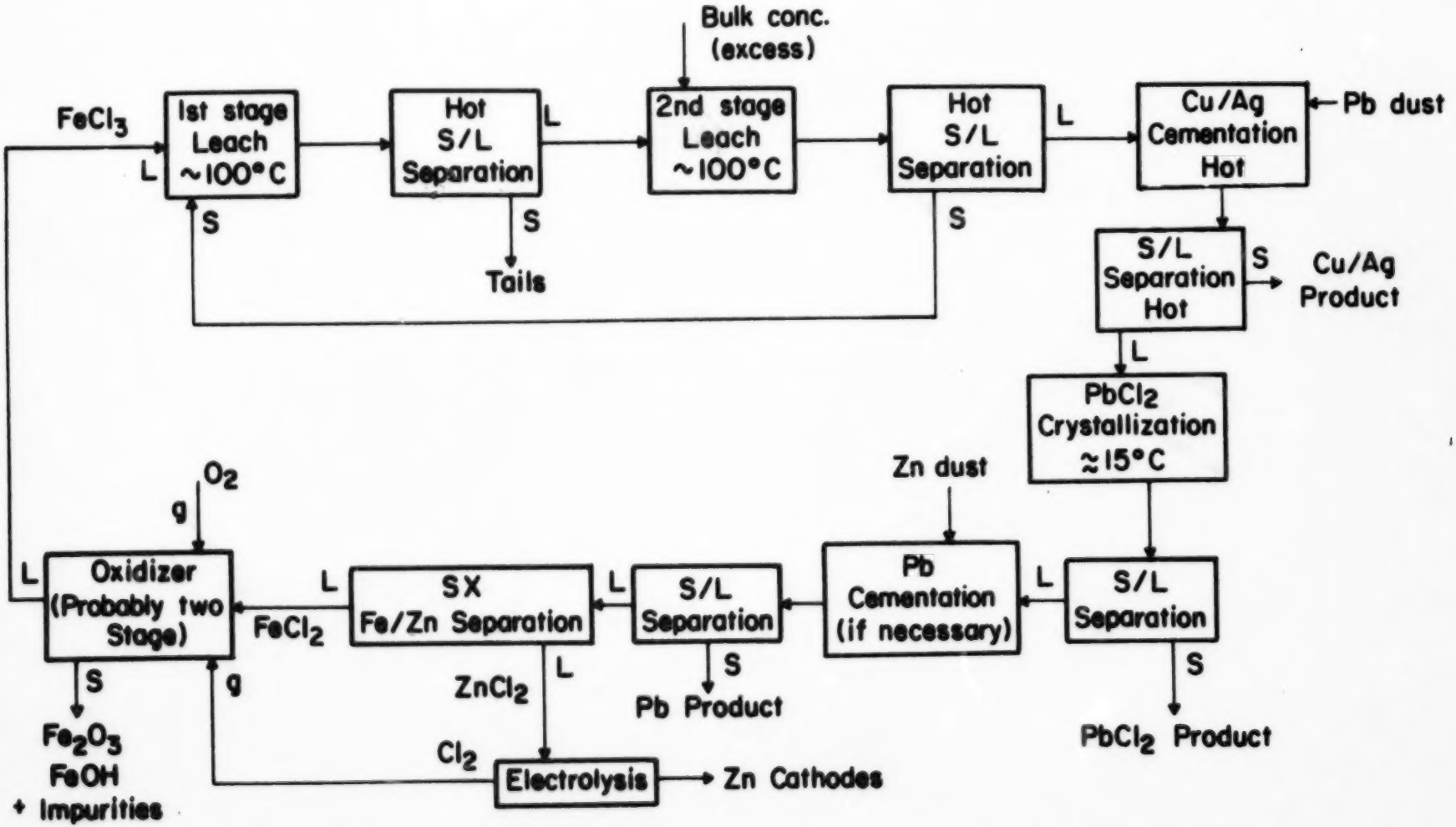

FIGURE 1: Proposed Ferric Chloride Leach Process Flowsheet

In a second-stage leach, a smaller amount of fresh concentrate was added to the leach liquor from Stage I to reduce the residual 1.5 g/L ferric ion. Conditions used were:

Volume preg = 29 L
Concentrate = 4.54 Kg
Temperature = 103°C
Retention = 2 h

First-stage extractions obtained from this leach were 99.6% Pb, 91.9% Zn, 90.1% Cu, 84.7% Ag and 21.9% Fe. These extraction figures as based on residue assays, are suspect as the leach slurry frothed and/or boiled over in each leach stage. This was found to be due to boiling caused by poor temperature control (B.P. slurry 108°C). Another problem was incomplete washing of the leach residue leaving residual Pb values reported as $PbSO_4$.

Second Pilot-Plant Leach

The same 57 L leach vessel as used previously was employed. To overcome the lead solubility problem, 1 M NaCl was added to the leachant, and the concentrate to leachant ratio reduced. Since there were unleached metal values remaining in the residue in the first pilot plant, the ferric ion to concentrate ratio was also increased.

The second pilot plant leach conditions were:

Concentrate = 8.406 Kg
2 M $FeCl_3$ leachant - 52.0 L
HCl = 0.35 M
NaCl = 1 M
Temperature = 102-103°C
Retention = 6 h
Wash = 2-displac. washes - 1 L of 1 M NaCl each
2-displac. washes - 1 L of water each

The second stage leach (or the conditioning of the leach liquor to reduce residual ferric ion) was abandoned due to the precipitation and loss of soluble copper as experienced in the first pilot plant.

Temperature control was good, averaging 103°C. Metal extractions were 99.8% Pb, 99.5% Zn, 98.3% Cu, 93.6% Ag and 39.7% Fe. Unfortunately, because of the difficulty in solubilizing anhydrous $FeCl_3$, the resulting leachant contained 1.275 times the stoichiometric $FeCl_3$ rather than 1.1. Undoubtedly, the excess ferric ion and increased retention time improved the metal extraction considerably. The metal extraction over the 6 h leach, shown in Figure 2, indicates that 6 hours were needed for maximum Zn and Ag recovery. However, this pilot plant did serve to indicate that it was possible to obtain over 95% extraction of the Pb, Zn and Cu. Considerable iron was also extracted but residual Ag remained refractory possibly due to it being in refractory tetrahedrite. The leach liquor however, contained 13 g/L ferric ion.

To overcome the problem of reducing residual ferric ion to zero level and also to maximize metal extractions, further bench work was performed utilizing a two-stage countercurrent leach. In the first stage, leach liquor from the second stage leach containing some ferric ion would leach the fresh concentrate while the first stage leach residue would be attacked by freshly re-constituted ferric ion liquor recycled from solution purification.

BENCH-SCALE LEACH TESTS - B

Ordinarily, the liquor containing principally ferrous ion and metal values from the $FeCl_3$ leach circuit would be processed through solution treatment to recover the metals; the solution would then be treated for excess iron elimination followed by chlorination to regenerate $FeCl_3$. A series of tests were performed to assess the feasibility of adding Cl_2 to the second stage of the leach whereby $FeCl_3$ would be simultaneously generated and consumed in a cyclic manner. The second stage leach liquor containing ferric ion and residual metal values would then be available for the first stage leach upon recycle. By adding Cl_2 to the leach the chlorination stage for regenerating the $FeCl_3$ recycle liquor would be eliminated.

Chlorine Assisted $FeCl_3$

In an exploratory test, 162 g of bulk concentrate were leached with one litre of approximately 2 M Fe_T, at about 80 vol % Fe^{+3} to the 1st stage and 2 M Fe^{+2} to the 2nd stage. The temperature of the 1st stage was

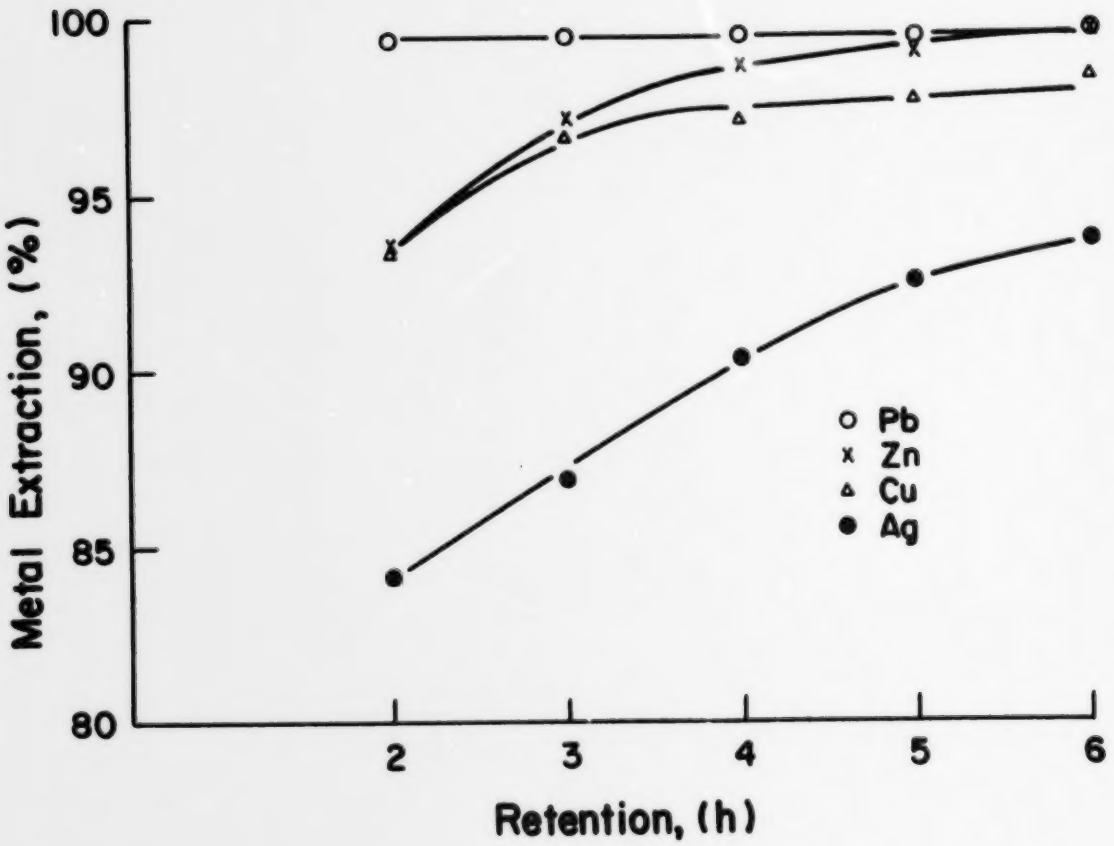

FIGURE 2: Effect of Retention Time on Metal Extractions - PP2

102-103°C and 105°C in the 2nd stage. Retention time was arbitrary in the 1st stage at 2.5 h or such time as it took to reduce the redox potential of the leach liquor to 300 mV with respect to platinum/calomel electrodes (Fig. 3). In the 2nd stage, Cl_2 was delivered at a maximum rate which necessitated 6.0 h retention. Cl_2 addition was equivalent to that which would be recovered from the Zn and Pb electrolyses. The redox potential was used as a control method. Conditions and results for these tests will be found in Table 2. Two cycles were completed whereby the leach liquor from Cycle 1, Stage 2, was the leachant for Cycle 2, Stage 1 leach.

Table 2. $FeCl_3$-Cl_2 leach

Cycle	Stage	OP Conditions							L.L.*		Extraction (%)				
		Fe^{+3} g/L	Fe^{+2} g/L	Zn g/L	T °C	Retent h	Cl_2 mL/min	Final EMF (mv)	Fe^{+3} g/L	SO_4 g/L	Pb	Zn	Cu	Ag	Fe
1	1	83.7	20.0		102.7	3	-	295	7.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1	2	3.5	111.6	1.47	104.6	6	71	470	43.2	n.a.	99.7	98.7	95.9	94.2	32.3
2	1	101.9**	1.5	5.97	102.5	3	-	274	2.8	25.4	n.a.	n.a.	n.a.	n.a.	n.a.
2	2	5.6	112.5		104.2	3	71	524	68.4	n.a.	99.6	97.8	94.2	93.8	33.0

*Leach liquor
**Fe^{+3} increased from 43.2 g/L by further Cl_2 addition
n.a. - not available

It can be seen from Table 2 that the Cl_2-assisted $FeCl_3$ leach did effect good metal extraction although Cu and Ag extractions remain around 94%. In pilot plant #1, 6.2 g SO_4/L was generated in the leach liquor and in pilot plant #2, 8.5 g SO_4/L was formed. In the Cl_2-assisted leach test, SO_4 reached a level of 25.4 g/L. In considering in-situ $FeCl_3$ leaching with Cl_2, the net SO_4 generated by chlorination is excessive. Sulphate generation must be considered since SO_4 follows the $PbCl_2$ crystals and is an undesirable $PbCl_2$ impurity.

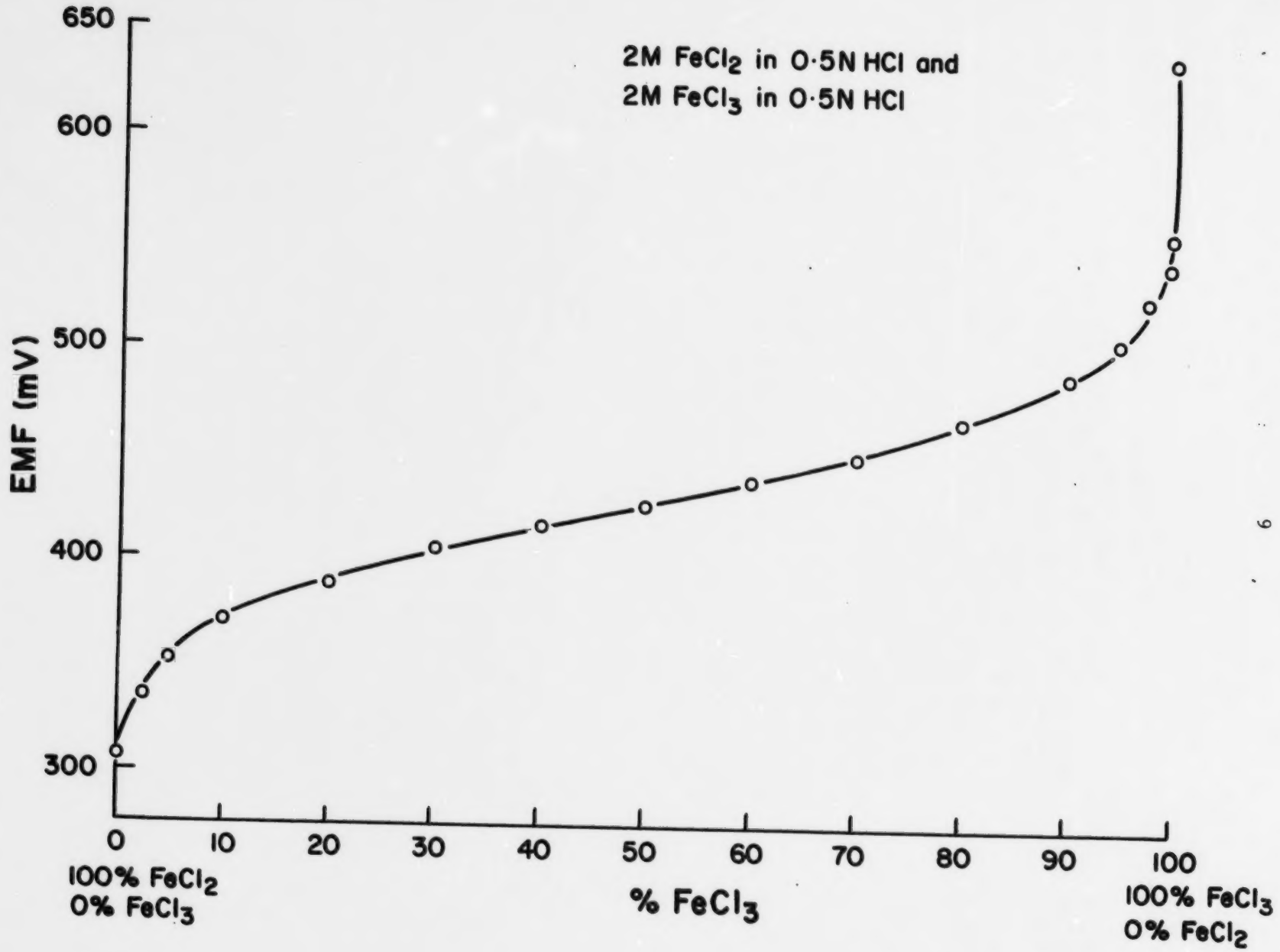

FIGURE 3: Calibration Curve for the Oxidation of Ferrous Chloride to Ferric Chloride

In the next two tests, a single stage leach was done with Cl_2 addition. One test had 25 g Fe^{+2}/L only added while the other test had no iron. These tests were done to check the leaching ability of Cl_2 alone versus the cyclic Fe^{+2}-Fe^{+3}-Cl_2 leach. All other leach conditions were constant at 102-103°C for 6 hours, under a N_2 atmosphere. Nitrogen was used in an attempt to reduce SO_4 formation via air oxidation. The metal extractions were as follows:

	Fe^{+2}/Cl_2	Cl_2
Pb	95.3%	72.7%
Zn	95.3	90.3
Cu	92.0	80.9
Ag	93.7	88.8
Fe	32.0	33.9

Residual ferric ion and sulphate in the leach liquor were 19.1 g Fe^{+3}/L and 19.95 g SO_4/L, for the Fe^{+2}/Cl_2; 8.6 g Fe^{+3}/L and 23.61 g SO_4/L for the Cl_2 alone. This would indicate that the Cl_2 does increase the formation of SO_4. However, the Fe^{+2}/Cl_2 cycle does generate Fe^{+3}. The Fe^{2+}/Cl_2 technique can give good metal extraction at low Fe concentrations, (eg. 25 g/L), and in two stages would give excellent extractions and possibly encourage low residual Fe^{+3} ion in the first stage leach liquor. To this end a series of two-stage leach tests were carried out using decreasing iron concentrations in the lixiviant. The results are shown in Table 3. A N_2 atmosphere was used in all these leach tests.

Table 3. Effect of ferric ion level in $FeCl_3$-Cl_2 leach

Stage	Operating Conditions					L.L.		Extraction (%)				
	Fe^{+3} g/L	Fe^{+2} g/L	T °C	Retent h	Cl_2 mL/min	Fe^{+3} g/L	SO_4 g/L	Pb	Zn	Cu	Ag	Fe
1	97.7	0.001	103.6	6.0		6.9	2.23					
2	2.4	97.1	105.0	1.58	71	33.9	14.71	99.8	97.7	91.7	93.4	33.0
1	77.7	0.012	102.4	2.0		7.9	1.66	99.3	73.5	66.9	79.8	15.7
2	1.8	73.7	104.7	6.17	71	78.4	18.52	99.6	98.2	90.1	95.3	33.6
1	51.4	0.005	103.0	1.0		2.7	1.14	99.1	52.5	26.0	59.2	12.4
2	1.5	50.0	103.7	6.0	71	52.0	15.22	99.4	91.6	(78.0)	87.7	27.9
1	25.8	0.002	103.5	1.0		0.6	0.0	98.7	24.5	8.9	27.6	0.0
2	0.6	23.2	102.8	6.0	71	29.6	18.13	99.3	95.9	93.0	95.6	45.2

It is observed that a N_2 atmosphere does not inhibit SO_4 generation. Furthermore, increasing initial Fe^{+3} concentration in the first stage increases the SO_4 formed (Fig. 4). According to the amount of Cl_2 delivered in these leach tests, SO_4 is generated stoichiometrically in the second stage according to the equations given in ref. 15:

$$Cl_2 + H_2O \rightarrow HOCl + HCl \quad (1)$$

$$4HOCl + MS \rightarrow MCl_2 + 2HCl + H_2SO_4 \quad (2)$$

It can be also seen from the data in Table 3 that there is not any real trend to better overall metal extractions with increasing initial Fe^{+3} ion concentration. But it can be said that this two-stage leach does improve metal extractions over that realized in the first pilot plant and that lowering the iron in the lixiviant does realize lower residual ferric ion in the 1st stage leach liquor.

It was thought that possibly increased HCl concentration in the leachant may inhibit sulphate formation (Eq. 1 and 2)(14,15). The results of a series of two-stage $FeCl_3$-Cl_2 leaches are shown in Table 4. Conditions used were 2 h retention, 1st stage 25 g/L Fe^{3+}, 102-103°C; 2nd stage 25 g/L Fe^{2+}, 6 h of Cl_2 at 103-104°C.

Table 4. Effect of HCl concentration on sulphate formation

1st stage		2nd stage	
HCl (g/L)	SO_4 (g/L)	HCl (g/L)	SO_4 (g/L)
16.8	0.0	0.1	24.21
36.1	0.18	28.4	3.72
54.7	0.07	44.4	11.52

As usual, apart from SO_4 contained in the concentrate feed, essentially all of the fresh SO_4 is generated in the 2nd stage. The increase of HCl concentration would seem to indicate that in fact SO_4 generation is reduced. The value of 3.72 g SO_4/L is however suspect since metal extractions were significantly lower in that leach. More work is necessary to confirm the effect of HCl concentration on sulphate formation.

Direct Two-Stage $FeCl_3$

Although the $FeCl_3$-Cl_2 2-stage leach did show promise with much improved metal extractions and a low residual ferric ion (using 25 g Fe^{+3}/L) in the first stage leach liquor, sulphate generated does remain a problem to solve. Therefore, attention was turned to direct two-stage $FeCl_3$ leaching. In the selection of leach conditions, it was considered that only sufficient iron in the lixiviant is needed to react with the Cl_2 recycle from product recovery. It was also possible to have low or high ferric ion to the first stage leach. Low ferric concentration hopefully would react completely with the fresh concentrate to produce lower Fe^{3+} solution values. Conditions for the leach series are as follows:

Stage I - Bulk concentrate = 202.5 g
Lixiviant = 1.25 L with 1 M NaCl, 0.43 HCl
$FeCl_3$ = variable conc g/L
Temperature = 103-104°C
Retention = 3.0 h

Stage II - Feed = Stage I leach residue
Lixiviant = 1.25 L with 1 M NaCl, 0.43 M HCl, 80 g Fe^{+3}/L
Temperature = 105°C
Retention = 4.5 h

The results will be found in Table 5.

Table 5. The effect of Fe^{+3}/Fe^{+2} ratio in lixiviant on metal extractions in $FeCl_3$ - 2-stage leaching

1st Stage Lix		1st Stage Extraction (%)						1st Stage Preg		2nd Stage Lix	2nd Stage Extraction (%)					
Fe^{+3} g/L	Fe^{+2} g/L	Pb	Zn	Cu	Ag	Fe	S SO_4	Fe^{+3} g/L	Fe^{+2} g/L	Fe^{+3} g/L	Pb	Zn	Cu	Ag	Fe	S SO_4
36.6	47.6	98.9	33.4	24.1	57.0	5.5	0.0	5.30	85.0	76.8	99.4	96.1	85.7	92.1	24.8	2.06
44.8	38.3	91.1	40.9	31.2	47.9	7.7	0.0	6.30	80.2	79.6	99.6	94.7	83.0	90.7	29.6	2.37
50.0	28.8	99.2	51.3	33.8	60.0	6.9	0.04	5.7	81.7	79.6	99.4	94.5	77.5	91.0	29.4	2.86
62.3	19.6	99.2	61.7	49.6	65.2	10.6	0.4	5.0	83.2	84.5	99.5	92.4	79.3	92.0	31.2	3.60
79.5	0.04	99.2	81.1	75.5	80.3	18.6	0.0	0.9.	86.1	80.9	99.6	97.5	86.8	94.0	41.1	5.9

Extractions were very encouraging for Pb, Zn and Ag. However Cu extraction was quite low at 78-87%. A check of the copper distribution indicated that in cases where there was considerable soluble Cu recycle, precipitation of Cu occurred upon contact with fresh concentrate. Where copper extraction is maximized in Stage I, low levels of soluble copper recycle do not result in copper precipitation. This would suggest the use of maximum metal extractions in Stage I. Another point in these data is that at lower levels of ferric ion in the Stage I lixiviant, the resulting sulphate is lower out of Stage II. This confirms the observation made in the $FeCl_3$-Cl_2 2-stage leach (Fig. 4). The iron extraction also increases as Fe^{+3} concentrate increases in the lixiviant. The increase in iron extraction coupled with the observation on increasing SO_4 formation, suggests that pyrite is the mineral from which SO^{+} is generated (13).

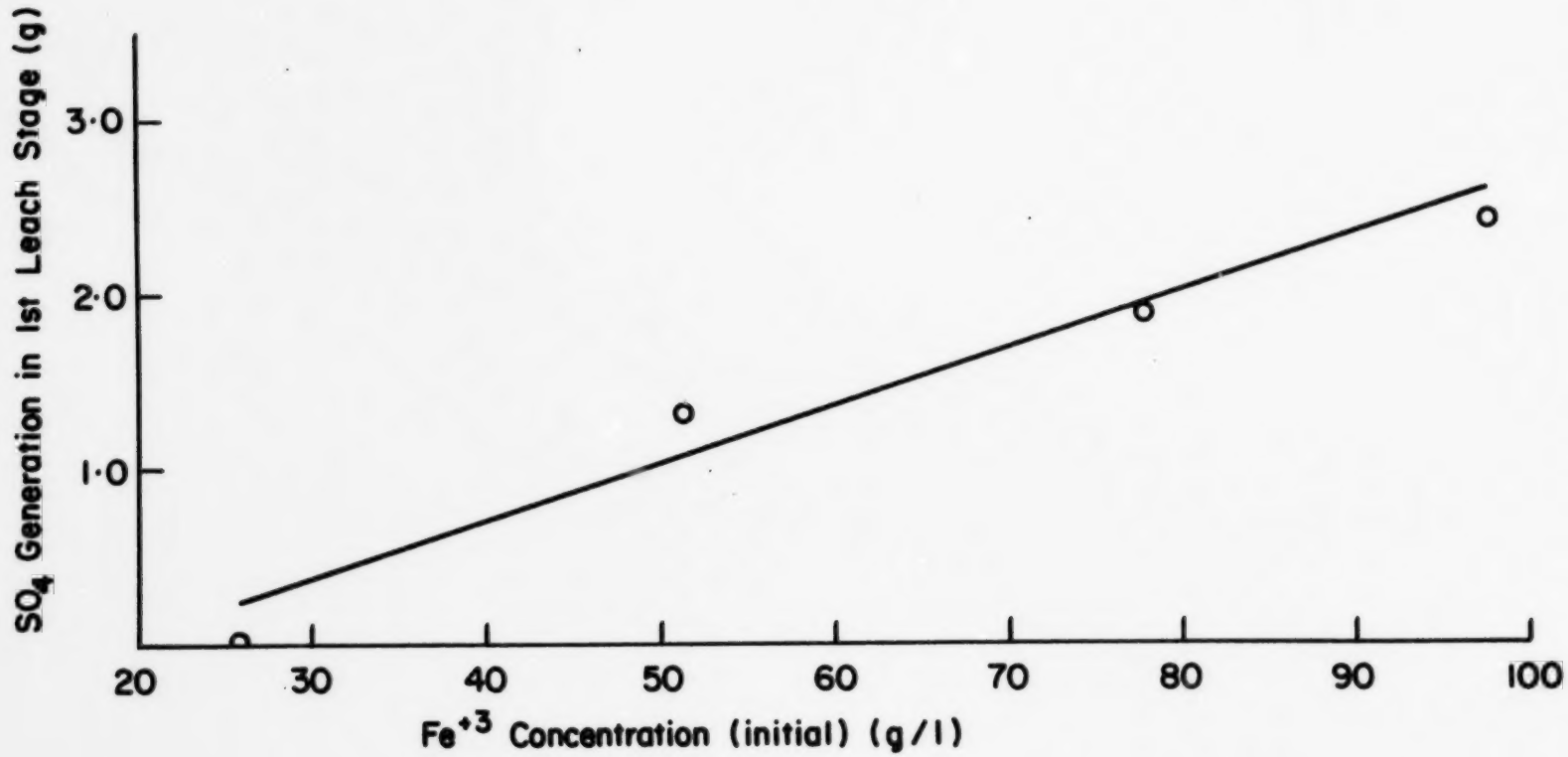

FIGURE 4: Net $SO_4^{=}$ Generation in 1st Leach Stage as Function of Initial Fe^{+3} Concentration

It is also interesting to note that residual ferric ion at approximately 5 g/L remained in the leach liquor out of all tests except the 80 g Fe^{+3}/L with only 0.04 g Fe^{+2}/L lixiviant. Here the residual Fe^{+3} out of Stage I was only 0.9 g/L. The other leach tests had substantial Fe^{+2} in the lixiviant. The same observation can be made of data in Table 4. It would seem that one way to drive the residual Fe^{+3} down to the order of 0.5-1.0 g/L is to avoid recycling Fe^{+2} values to Stage I.

It has been considered that elemental sulphur may interfere with metal extractions. Therefore a test was done utilizing perchloroethylene to remove S° from the surfaces of Stage I leach residue. Results will be found in Table 6.

Table 6. The effect of S° on second stage of leaching

Lixiviant (g/L)			Leach Liquor	S° Removal	Extraction (%)					
1st Stage		2nd Stage								
Fe^{+3}	Fe^{+2}	Fe^{+3}	Fe^{+3} g/L		Pb	Zn	Cu	Ag	Fe	S_{SO_4}
36.4	40.2	76.8	3.3	yes	99.5	92.4	91.3	95.1	33.9	2.72
36.6	47.6	76.8	5.3	no	99.4	96.1	85.7	92.1	24.8	2.06

It is apparent that the removal of S° from the leach residue does improve metal extractions; especially of Cu and Ag which with iron are contained in the most refractory minerals. However, the generation of SO_4 is also increased substantially.

The precipitation of recycled soluble copper is a problem in two-stage $FeCl_3$ leaching. It was thought that maybe Cu^+ is present and being precipitated. Therefore, lixiviants were made up containing Fe^{+2}, Fe^{+3} and either ≈2 g Cu^+/L or ≈2 g Cu^{+2}/L. Results will be found in Table 7. One stage leaching of fresh concentrate was used.

Table 7. Effect of copper ion valency in precipitation of copper

1st Stage Lixiviant (g/L)				Leach Liquor (g/L)				Extraction (%)				
Fe^{+3}	Fe^{+2}	Cu^{+}	Cu^{+2}	Fe_T	Fe^{+3}	Fe^{+2}	Cu	Pb	Zn	Cu	Ag	Fe
62.3	19.6	0.0	0.0	88.2	5.0	83.2	0.59	99.2	61.7	49.6	65.2	10.6
63.9	21.1	2.18		94.9	10.4	84.5	2.89	99.0	63.7	64.4	70.0	12.1
65.0	20.6		1.74	93.9	5.80	88.1	2.54	99.1	67.2	69.8	71.9	14.7

The readily available Cu^{+2} acted as a leachant and with the Fe^{+3} improved extraction considerably over Fe^{+3} alone, while Cu^{+} improvement of metal extraction was intermediate. No precipitation of Cu took place which suggests that the concentrate alone does not cause copper precipitation but that one or more of the other soluble metal values which are recycled causes the precipitation (14). More testwork in this area is necessary.

All the preceding tests suggested a new design to the two-stage leach:

1. Low initial Fe^{+3} in the 1st stage lixiviant to minimize sulphate formation and promote minimum residual Fe^{+3} in the leach liquor.
2. No initial Fe^{+2} ion in each lixiviant which promotes the reduction of all of the Fe^{+3}.
3. Because of the amount of iron which is leached, increase the quantity of Fe^{+3} to 100 g Fe^{+3}/162 g bulk concentrate from 80 g.
4. Recycle Cu^{+2} to avoid copper precipitation and to improve metal extraction (11).
5. Increased leach temperature to improve Cu, Ag extraction (5,11).

To eliminate Fe^{+2}, Cl_2 was added to the recycle lixiviants: about 50% to each stage. The recycle liquor to the 2nd stage would contain 50 g Fe^{+3}/L. The liquor out of the 2nd stage for recycle to the 1st stage would contain 50+ g Fe_T/L. The oxidation of the $FeCl_2$ in the recycle liquor to eliminate leached Fe will generate some Fe^{+3}. Thus the Cl_2 distribution to the two liquors can be adjusted to obtain 100% Fe^{+3} in each lixiviant.

Results from a leach test indicated that the loss of the Fe^{+3} driving force usually provided to the 2nd stage by the one-stage chlorination of 100 g Fe/L caused poor metal extractions. Therefore, the leach

temperatures were increased by increasing the NaCl concentration from 1.0 to 3.5 M in the recycle lixiviant. The addition of NaCl would also help Pb, Ag and Cu solubilities. The results of these leach tests are found in Table 8. General conditions are as follows:

Stage I - Charge = 202.5 g bulk concentrate/1.25 L
Lixiviant = 3.5 M NaCl, 0.43N HCl, 50 g Fe^{+3}/L
Retention = 3 h

Stage II - Lixiviant = 50 g Fe^{+3}/L, 3.5 M NaCl, 0.43N HCl
Retention = 4.5 h

Table 8. Elimination of Fe^{+2} in lixiviants and the effect of temperature

Cycle	Stage	OP Conditions		Leach Liquor		Extraction (%)				
		Fe^{+3} g/L	Temp °C	Fe^{+3} g/L	SO_4 g/L	Pb	Zn	Cu	Ag	Fe
1	1	50.4	103.3	0.80	10.1					
	2	50.4	103.5	5.60	3.87	99.6	92.6	79.0	89.4	28.9
2	1	59.2	103.1	1.3	13.52	99.3	59.6	51.2	64.5	9.9
	2	50.0	103.6	7.5	5.04	99.5	96.5	84.4	89.1	32.1
1	1	49.7	106.7	1.3	9.72	99.0	54.2	48.7	66.6	11.6
	2	45.8	106.9	7.7	2.58	99.5	96.3	86.7	91.6	28.3
2	1	44.4	107.6	1.20	11.01	99.0	48.3	43.9	66.6	9.8
	2	50.0	107.7	4.40	1.98	99.5	98.4	93.3	87.1	26.9
3	1	45.8	108.2	0.0	12.18	99.0	52.7	49.1	63.6	
	2	48.1	108.0	6.0	2.70	99.5	98.3	93.9	91.6	

DISCUSSION ON LEACH

There were three factors to consider in optimizing the leach process:

maximize metal extractions,
eliminate residual ferric ion in the leach liquor,
eliminate sulphate formation.

High residual Fe^{+3} in the leach liquor increases costs in cementation and causes an undesirable iron impurity level in the $ZnCl_2$ electrolyte. It was found by experimentation that low initial ferric ion and the elimination of initial ferrous ion in the lixiviant allowed the residual ferric ion in the recycle leach liquor to be reduced to a range of 0-1.3g/L. Then one-stage chlorination of recycle $FeCl_2$ liquor was revised by applying Cl_2 to each liquor entering a leach stage. This may require extra Cl_2 in the initial stages of continuous leach operation but should balance in due time with $FeCl_3$ formation from the oxidation stage used to eliminate excess iron. The stoichiometric Cl_2 from recycle can be split proportionately to oxidize 50 g Fe^{+3}/L entering the 2nd leach stage and 50 g Fe_T plus/L out of the 2nd leach stage.

It has been found that low initial Fe^{+3} added to a leach stage reduces sulphate formation. High initial ferric ion does improve metal extractions considerably but by attacking pyrite which increases sulphate formation (Jackson and Strickland, 1958, ref. 13). Certainly, with proper attention, some sulphate formation during ore grinding, flotation and storage can be eliminated. However, there will always be sulphate formed to some degree in the leach. If some of the sulphate follows the $PbCl_2$ crystallization stage, this may be a way to eliminate sulphate. $PbCl_2$ could be dissolved and sulphate removed by $CaCl_2$ or by jarosite precipitation. Testwork suggested that increased HCl concentration in the leach may reduce sulphate formation but poses the problem of increasing costs in the cementation step.

The particle size of the concentrate feed is very fine and therefore grind was not varied. Zinc and lead, at optimum leach conditions, are readily extracted at 95%. Copper and silver are more refractory although copper is more amenable to extraction at 95% as indicated in PP 2. Silver will only extract to 94%. A mineralogical analysis of a leach residue indicated that the silver is contained in tetrahedrite. There is a residual 30-50 ppm of Ag which has a value of about $10 per metric ton of residue. Before resorting to a different leach process to reduce this Ag loss, leach residue will be screened into fractions to find if there is a concentration of Cu and Ag in the coarse fractions. This coarse fraction could then be recovered, reground, and recycled back through the leach circuit. Failing this, an alternative process will have to identified to further extract silver from the leach residue.

An increase in temperature definitely helped the metal extraction. It is interesting that Elkem a/s of Norway leach at 105-115°C (11). It is not reported as to how Elkem reach 115°C, but in our case, to proceed with an atmospheric leach using a low level of Fe^{+3} ion, NaCl was added to increase the leach temperature. Of course, besides increasing the allowable leach temperature to 108°C, NaCl addition does improve Pb, Ag and Cu solubilities. Using low Fe^{+3} ion lixiviant at a leach temperature of 103°C as compared to 108°C did give relatively low metal extractions. However, the elevated temperature compensated for this. As has been previously explained, low Fe^{+3} ion concentration and high leach temperature give more advantages than high ferric ion concentrations.

Although S° elimination between leach stages did improve metal extractions, it would be a costly step and does increase SO_4 formation. The parameters as developed compensate for the presence of S°. Soluble copper precipitation in the leach circuit has been eliminated possibly by inter-stage chlorination or by the low level of copper in the recycle liquor. Certainly it is not necessary to maximize metal extractions in the 1st stage of leaching by high Fe^{+3} in the lixiviant.

Retention time in each of the two stages of leaching has not been optimized at this time. It is very possible that the retention can be reduced from 4.5 h (1st stage) and 3 h (2nd stage) to possibly 2 h in each stage as found by other investigators (11). This aspect of the leach investigation will be completed shortly. The liquid-solid ratio will also have to be optimized.

LIQUID/SOLID SEPARATION AND WASHING

The following is abstracted from Dutrizac (5) concerning bench-scale leach tests:

"Although the bulk concentrates themselves, especially the second batch, were very fine grained, the leach residues settled and filtered fairly well without the use of flocculants. There are likely two reasons for the favourable settling properties. Firstly, the extremely fine particles are likely dissolved during the leaching period and this would leave the coarser grains which would settle better. Secondly, the elemental sulphur reaction product at 102°C is "sticky" and tends to agglomerate all the particles into coarser, easily filtered grains. The time to filter 2 L of hot leach slurry (with ~190 g leach residue) on a

24-cm diameter Buchner vacuum filter was 85-90 s. The calculated average filtration rate was then 0.051 mL/cm^2 . s; that is, the filtration rate is greater than 2,000 kg/m^2 . h.

The residues were readily washed with 95-100°C water to remove entrained salts or $PbCl_2$ crystals. Since the lead content of the residue reflects mostly $PbCl_2$ plus minor unleached PbS, it is probably a good indicator of the washing efficiency. The following data show the lead concentration of the residue after washing with incremental amounts of hot (100°C) water.

Wash Water	% Pb in Residue
0 x 200 mL	0.59
1 x 200 mL	0.16
2 x 200 mL	0.30
3 x 200 mL	0.12
4 x 200 mL	0.14

The relatively high lead content (0.59 wt %) of the filtered but not washed residue indicates entrainment of the pregnant solution with its associated $PbCl_2$. The 0.12-0.14% Pb values of the well-washed residues probably reflect the residual PbS values. Within this framework, it is apparent that only one or two 200 mL washes would be needed to remove the entrained solutions; i.e. the filtration water (or recycled solution) demand is only 5-10% of the leach volume.

It would likely be desirable to thicken the hot leach residues either before hot filtration or for recycle to a second stage of leaching. Standard settling tests were done using a 2000 mL graduated cylinder to ascertain both the settling rate and the relative clarity of the supernatant liquid. These tests were complicated by the crystallization of $PbCl_2$ that commenced at about 85-90°C for leaching done under the preferred conditions. After 5 min of settling, it appeared that all the solids had settled to 240 mL of pulp leaving behind a cloudy fluid. After 20 minutes, the temperature had fallen to 87°C and $PbCl_2$ crystal formation in a relatively clear fluid commenced. Ater 50 minutes the solution was clear except for a "rain" of relatively coarse $PbCl_2$ crystals; the volume of the pulp was about 228 mL. After 48 h, the fluid was clear, and the sulphide pulp (225 mL) was covered by about 100 mL of $PbCl^2$ crystals.

The above observations suggest that the thickening and filtration of the hot slurries should be relatively simple; the major problem will be to ensure that the system remains above the crystallization temperature for $PbCl_2$."

PILOT PLANT I

The leach slurry was discharged by gravity to a 44-cm diam rubber-coated pan filter which had a cover fitted to allow pressure filtration. The unit was insulated to maintain a slurry temperature of about 90°C so as to maintain $PbCl_2$ solubility. Washing was effected by the application of 3 batches of 5 L H_2O at 90°C.

Observations

The slurry filtered very quickly but the washing was poor. On inspection it was found that the center of the cake was very thin allowing short-circuiting of the wash water. Considerable $PbSO_4$ and $PbCl_2$ crystals remained in the residue.

PILOT PLANT II

To correct the above problems, a deflector plate was placed in the center of the pan filter to overcome the short-circuiting. The washing technique for the second pilot plant was changed to 2-1 L displacement washes of 1 M NaCl followed by 2-1 L displacment washes of water, all at 90°C. The washing efficiency is plotted in Figure 5.

Observations

It is obvious that displacement washing was efficient for Ag, Cu, Fe and Zn but was short of sufficient stages. However, elimination of soluble Pb was less efficient. The data suggest that a hot repulp in a brine solution stronger than 1 M NaCl may be necessary followed by displacement washes. It was calculated that there were approximately 3 L of leach liquor to displace. Only 4 L of wash water were used which would indicate that the leach residue is easily washed. Because of the close water balance requirements for a leach circuit using a recycle liquor, wash water

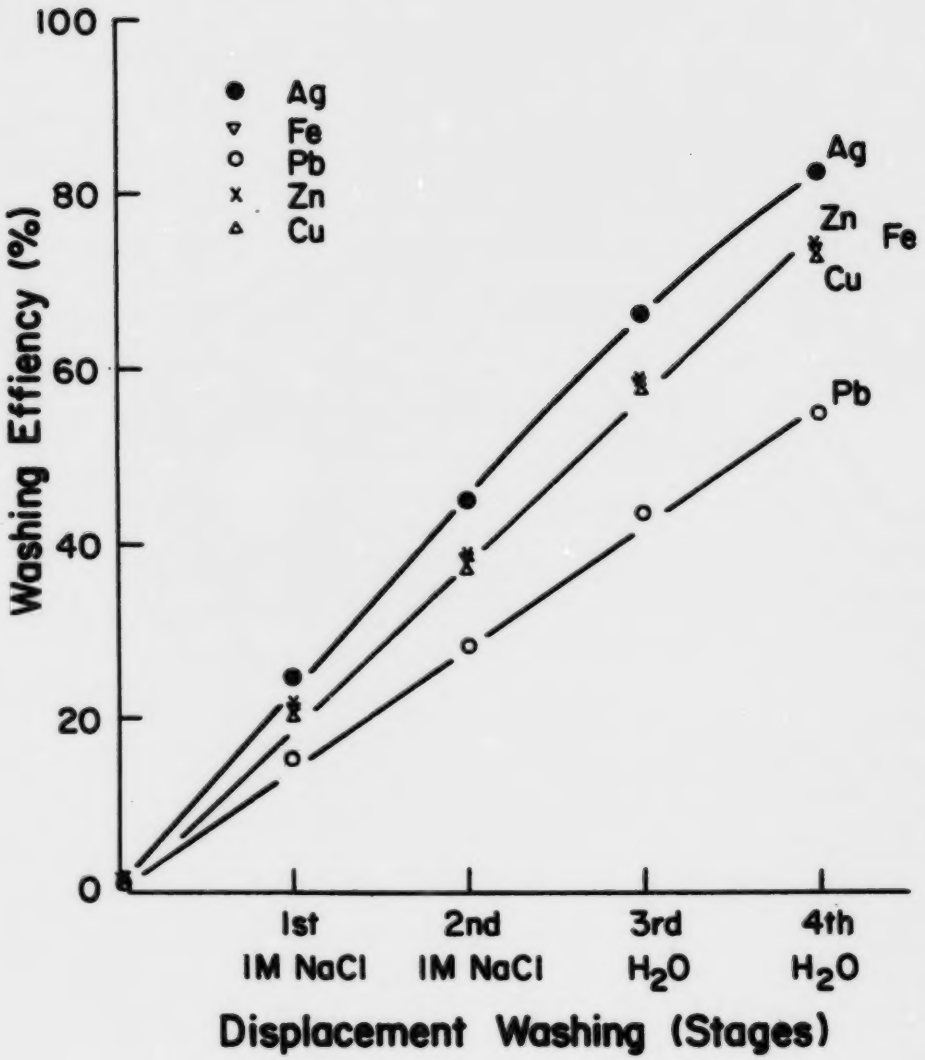

FIGURE 5: Displacement Washing Efficiency in Pilot Plant II

was minimized. The wash water was added to the leach liquor and evaporation used to maintain the water balance.

CEMENTATION

FIRST PILOT PLANT

Conditions for the cementation of Cu and Ag from $FeCl_3$ leach liquor were obtained from MacKinnon of CANMET (16,17). Fine Pb° powder was used as it was found to be much more active than granular Pb°. It was estimated that 125 g Pb° (4X stoic.) would be needed with one hour retention at 90-100°C and a N_2 atmosphere. The temperature was held at 90°C rather than 70°C to maintain $PbCl_2$ solubility. In the pilot operation, spills and Cu-Ag precipitation resulted in less Cu-Ag values to be cemented out. The subsequent Pb° addition was not 4X but 15X the stoichiometric amount.

Table 9. Cementation of Cu and Ag from $FeCl_3$ leach liquor using Pb powder

Product	Vol L	Wt g	Pb	Zn	Cu	Ag	Fe_T	S/SO_4	pH	EMF
Init. Liq. g/L	29		2.67	54.7	0.15	0.033	126.6	5.52	0.0	305
Fin. Liq. g/L	27		1.74	57.3	0.006	0.0005	129.6	5.22	0.0	270
Cement Prod. %		47.1	55.39	1.02	5.31	1.45	1.99	1.21*		

*S_T

The results in Table 9 indicate that Ag is cemented out satisfactorily but Cu remains a little high and could contaminate the Zn strip liquor from SX. At this time it is not known whether Bi and Cd should be taken out at this stage. It might be possible to extract Zn from Bi and Cd satisfactorily in the SX stage and thus allow Cd and Bi build up on $FeCl_3$ recycle before separating them. Due to other priorities the second pilot-plant campaign was not extended to the solution purification step.

LEAD CHLORIDE PRODUCT

In the first pilot-plant campaign the leach liquor was cooled rapidly after cementation with the result that very fine $PbCl_2$ crystals formed which were difficult to handle. To increase the $PbCl_2$ solubility 1 M NaCl was added to the leachant for the second pilot plant, and leach liquorcooled slowly so as to increase $PbCl_2$ crystal size. The lead product was washed with saturated $PbCl_2$ solution.

The following procedure was used:

$PbCl_2$ = 465.9 g
Displacement wash = 4 x 250 mL
sat $PbCl_2$ solution

The dried product after the washing had a light brown stain possibly due to entrained iron. The crystals were repulped in 800 mL followed by 2 x 250 mL displacement washes with $PbCl_2$ solution.

The purity of the $PbCl_2$ crystals was as follows:

SO_4 = 7.113%
Zn = 0.005%
Cu = 0.0001%
Ag = 0.0001%
Fe = 0.0001%
Cd = 0.0001%
Bi = 0.0001%

It is obvious that the sulphate content is a serious problem because of its deleterious effect in fused salt electrolysis of $PbCl_2$ (18,33). Considerable sulphate resulted from oxidation of the bulk concentrate prior to leaching, and some sulphate forms during leaching. Although sulphate formation in the concentrate can be minimized and efforts are being made to reduce sulphate from leaching, there will always be sulphate.

It is possible that impure $PbCl_2$ could be re-dissolved and the sulphate separated by such means as IX, SX, precipitation or

recrystalizing from an adjusted solution using for example $CaCl_2$, HCl or Cl_2, or the limiting solubility of $PbSO_4$ versus $PbCl_2$. One could use aqueous $PbCl_2$ electrolysis (14) where the sulphate impurity may not be as serious a factor.

In the Clear process (20) (DUVAL), sulphate is removed by jarosite precipitation from the chloride recycle liquor. At CANMET considerable work has been done on jarosites (21,22,23,24,25). A necessity in jarosite precipitation is that the acid concentration be low (0.1 M HCl). This, of course, runs counter to the investigation of increased acid levels to suppress sulphate formation. If, in fact, sulphate follows the Pb and coprecipitates with $PbCl_2$ crystals, lead crystalization could possibly constitute a sulphate bleed, then an impure $PbCl_2$ solution could be treated by jarosite precipitation for sulphate removal. It is not known at this time to what degree the sulphate could be eliminated in this manner. No pilot-plant $FeCl_3$ recycle liquor has been treated as yet to control sulphate by jarosite precipitation. $CaCl_2$ addition has been suggested as another sulphate control method but $CaSO_4$ has considerable solubility in this chloride leach liquor.

The $PbCl_2$ crystals recovered from the second pilot plant had the following screen analysis:

	Wt %		Wt %
+ 297 µm	12.4	-105 µm + 74 µm	9.4
-297 µm + 210 µm	8.7	- 74 µm + 53 µm	6.4
-210 µm + 149 µm	10.5	- 53 µm	43.4
-149 µm + 105 µm	9.2		

ZINC RECOVERY

After Cu and Ag cementation and $PbCl_2$ crystallization, the $FeCl_2$-$ZnCl_2$ leach liquor from Pilot Plant I was treated by SX for Zn separation (26). There were problems and further testwork was done (27,28). This topic will be the subject of a separate report from the Solution Treatment Section.

ZINC ELECTROLYSIS

Some testwork on actual Zn strip liquor has been done but the results have not yet been formally reported. Zinc electrowinning from aqueous chloride electrolyte is proposed for the $FeCl_3$ process and work has been done by MacKinnon et al. at CANMET (29,30).

IRON REMOVAL BY OXIDATION

Leach liquor from SX (Pilot Plant I) was tested on the bench using the following conditions:

Temperature = 80°C
Oxidation = air
delivered by a glass frit with rapid agitation

The oxidation was very slow. After 4 hours 5.3 g Fe g/L had been removed from an initial concentration of 136.5 g/L. The desired iron level was 112 g/L. It was concluded that O_2 would be necessary.

The study of the oxidation of $FeCl_2$ was then taken up by Rolia of CANMET (31).

CHLORINATION OF $FeCl_2$ RECYCLE LIQUOR

Chlorination has not been done but is not considered a problem (32).

CONCLUSIONS

At this time the authors can only respond to their areas of interest, i.e., leach, L/S separation, cementation and $PbCl_2$ crystallization. The leach technique as proposed in this report (Figure 6) is well advanced and could be refined in a pilot-plant operation. This could also be said for L/S separation and cementation. Elimination of sulphate from $PbCl_2$ needs more benchwork. It is suggested that a suitable replacement for CANMET bulk concentrate could be bulk concentrate produced by Brunswick Mining and Smelting Co.

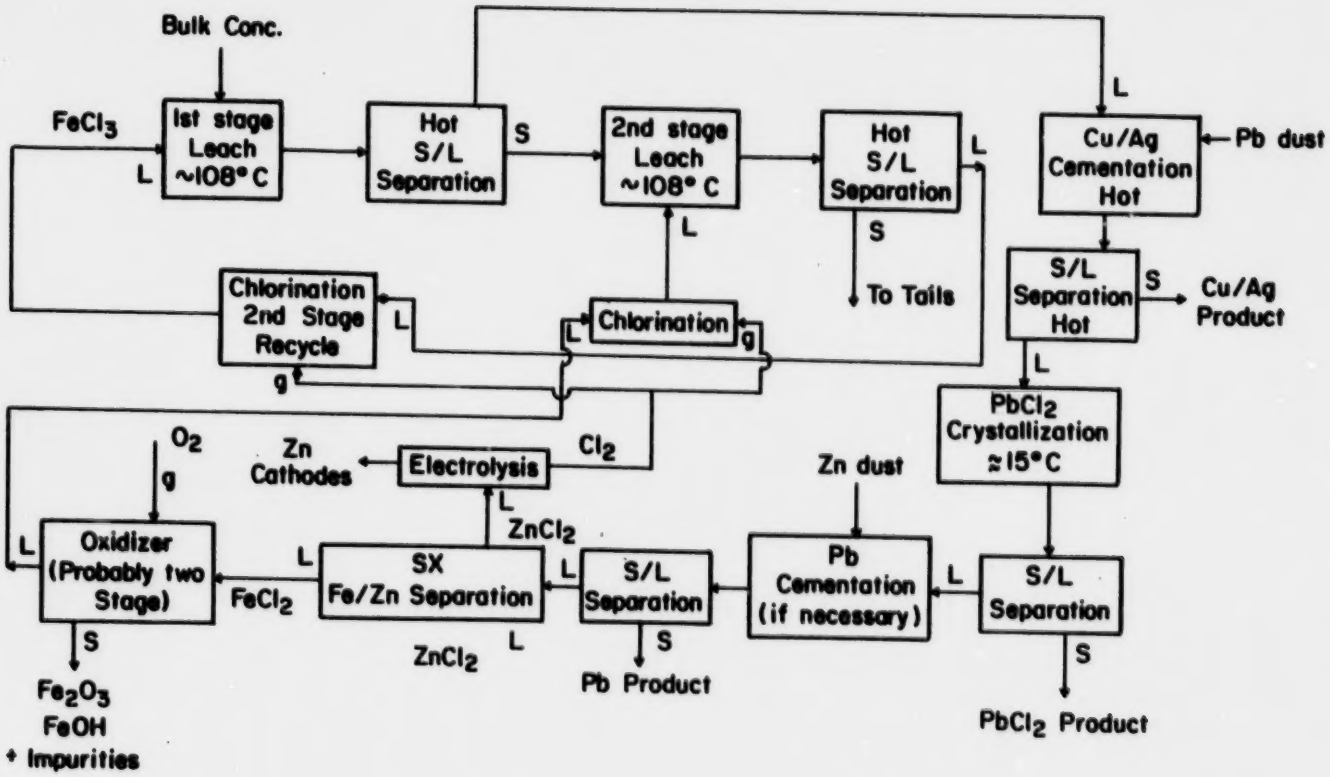

FIGURE 6. Proposed Two-Stage Ferric Chloride Leach Process Flowsheet

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